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(54) Title: REMOVAL AND RECOVERY OF SOLUTES PRESENT IN IONIC LIQUIDS BY PERVAPORATION

(57) Abstract: This invention refers to a method for the removal and the recovery of solutes present in ionic liquids, making use of the selective transport of solutes during pervaporation and employing adequate membranes. The invention aims at being utilised for the recovery of solutes present in ionic liquids, being its field of application the preparation and purification of ionic liquids, as well as the chemical, biochemical and biological reactions carried out in them. The process proposed consists of the selective transport of the volatile solutes dissolved in an ionic liquid across a dense, non-porous membrane, and their recovery on the opposite side of the membrane by means of a carrier gas or vacuum. Under favourable process operating conditions, it is possible to permit the selective transport of the desired solute(s) with an elevated permeation flux. Because of a lack of a measurable vapour pressure, the ionic liquids do not permeate across the membrane, remaining hence totally confined to the feed side.

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DESCRIPTION

REMOVAL AND RECOVERY OF SOLUTES PRESENT IN IONIC LIQUIDS BY PERVAPORATION

1 – This invention refers to a process for the removal and the recovery of solutes present in ionic liquids, making use of the selective transport of solutes during pervaporation and employing adequate membranes.

2 – The said invention aims at being utilised for the recovery of solutes present in ionic liquids, being its field of application the preparation and purification of ionic liquids, as well as the chemical, biochemical and biological reactions carried out in them. It also aims at the development of sensors and sample preparation techniques for analytical processes. The industrial domains covered are the chemical industry and industry of fine chemicals, bioconversions and biotechnology, environmental protection and environmental remediation, pharmaceutical and cosmetic industry, as well as food industry.

3 – Traditionally, industry employs solvents that due to their volatility contaminate the environment posing severe problems of pollution and safety. The toxicity, even at low concentrations, of some of the solvents, presents a serious threat in terms of environment and public health.

4 – Despite the significant efforts made in the development of techniques that allow diminishing the emission of these compounds into the atmosphere, the final result has not been satisfactory. Additionally, these processes for the retention and the capture of emissions require energy, which from the point of view of an integrated production cycle means and energetic waste, turning these overall production processes little environmentally friendly.

5 – Recently, the development of solvents was reported in literature that are capable of substituting these traditional solvents, providing the additional advantage of being practically non-volatile (K.R. Seddon, J. Chem. Biotechnol., 68, 351, 1997). These

solvents without any measurable vapour pressure do not evaporate and for this reason do not contaminate the environment.

6 – These solvents are usually designated “ionic liquids” (T. Welton, Chem. Rev., 99, 2071, 1999) because they are entirely constituted of ions, with the cation being commonly an organic cation and the anion commonly being an organic or an inorganic anion (C.L. Hussey, Pure Appl. Chem., 60, 1763, 1988; T. Welton, Chem. Rev., 99, 2071, 1999). Due to the fact that they are constituted entirely of ions, these liquids do not have a measurable volatility and are therefore considered an environmentally friendly alternative for traditional solvents (P. Wasserscheid and W. Keim, Angew, Chem., Int. Ed., 39, 3772, 2000).

7 – The traditional solvents can be substituted by ionic liquids in the most diverse areas, ranging from the use of a solubilization agent and the extraction of solutes, to the use in chemical reactions which might be electrochemical in their nature or catalysed by bio-catalysts, to the use as a thermofluid, the use in sensors and biosensors, and the use in the sample preparation for analytical purposes.

8 – In literature, it has been referred to the difficulty of removing and recovering solutes present in ionic liquids (M. Freemantle, C&EN, May 15, 37, 2000; P.B. McCormac and K.R. Seddon, Green Chem. 23, 1999). Despite all the potential advantages that ionic liquids inhere, it is necessary to provide methods capable of recovering solutes from ionic liquids in an environmentally clean way, in order to not cancel out the environmental advantages achieved by the use of these solvents.

9 – Processes proposed for the recovery of solutes present in ionic liquids are essentially distillation, extractions with aqueous media, the extraction supercritical carbon dioxide (A.E. Visser, R.P. Swatlowksi, and R.D. Rogers, Green Chemistry, 1, 2000; L.A. Blanchard and J.F. Brennecke, Ind. Eng. Chem. Res., 40, 287, 2001). Distillation is an energetically demanding processes as energy is not only applied in order to evaporate the solute(s) of interest, but also to the bulk ionic liquid which is practically non-volatile. Besides, if more than one solute is present in the ionic liquid, then the selectivity of the recovery is only determined by the vapour-liquid equilibrium of these solutes in the ionic liquid, which can be insufficient for achieving the desired degree of

separation of the solutes. The extraction by aqueous media is a process that can be considered clean if one pretends to transfer the solutes in an aqueous environment, but its efficacy is limited by the recovery of a restricted number of solutes. Supercritical carbon dioxide extraction (G. Brunner, Gas extraction, 1994, Steinkopf, Darmstadt; Springer, New York) is a process that can be considered environmentally clean, although it is technically demanding and involves elevated operation costs. Because during supercritical carbon dioxide extraction there exists a direct contact between the extraction fluid and the ionic liquid, it may be difficult to guarantee that there is no loss of ionic liquid into the supercritical fluid, which represents an important limitation of this technique.

10 – Recently, the recovery of butanol, present in the ionic liquid $[\text{omin}^+][\text{PF}_6^-]$, by pervaporation was described in literature, using a polydimethylsiloxane-membrane (A.G. Fadeev and M.M. Meagher, Chem. Commun., 295, 2001). The authors of this work report that pervaporation permitted the recovery of butanol present in $[\text{omin}^+][\text{PF}_6^-]$, however, conclude that the process is neither adequate nor advantageous with regard to other alternative processes, such as distillation. The authors of the work mentioned did not study the recovery of solutes using membranes of other materials, neither considered the recovery of solutes from other ionic liquids. They also do not refer to the recovery of solutes from ionic liquids resulting from chemical reactions which may be electrochemical or catalysed by bio-catalysts.

11 – Pervaporation is a selective membrane separation process which has been utilised for the recovery of dilute solutes from aqueous or organic bulk solvents. The major industrial application of pervaporation is the removal of water during the production of absolute ethanol (Membrane Handbook, Ed. W.S. Winston Ho and Kamalesh K. Sirkar, Chapman&Hall, chapter 10). Other applications of pervaporation have been mentioned in literature, such as the separation of organic compounds (idem), the recovery of organic solutes from aqueous media (idem), and the removal of water from organic solutions (idem).

10 – The present invention describes a novel process for the recovery of solutes, present in ionic liquids and possessing a measurable vapour pressure, by pervaporation with

membranes. For this process being efficient and for the recovery of the solutes desired occurring at elevated fluxes and in a selective manner, it is necessary to defined in an integrated way the system: solute(s) to be recovered/ ionic liquid/ pervaporation membrane/ operating conditions. Only in this integrated form it is possible to carry out the process for the removal and the recovery of the desired solute(s) with the desired selectivity, quantitatively and with elevated permeation fluxes across the pervapoation membranes.

13 – The major advantage and novelty of the present invention consists in the integrated utilisation of the pervaporation process in order to recover selectively one or several solutes present in ionic liquids, avoiding simultaneously the removal of the ionic liquid itself owing to its lack of a measurable volatility. If a membrane with adequate characteristics for a determined system solute(s)/ ionic liquid is employed, and if the appropriate operating conditions are applied, then this process permits recovering the desired solutes totally devoid of any ionic liquid, avoiding thus the loss of the latter into the environment.

14 – The pervaporation process consists of the selective transport of the chemical species, present in a liquid mixture or in a solvent, across a dense, non-porous membrane, and its recovery on the opposite side of the membrane by means of a carrier gas or vacuum. If the membrane was correctly chosen in terms of its physico-chemical properties, structure and thickness, it is possible to provide conditions that permit the selective transport of the desired solute(s) with an elevated permeation flux. Because of a lack of a measurable vapour pressure, the ionic liquids are practically not volatile and for this reason do not permeate across the membrane, remaining hence totally confined to the feed side.

15 – Figure 1 illustrates the removal and transport mechanism for a solute present in an ionic liquid. In this process (figure 1) a feed solution (2), comprising the ionic liquid and one or more solutes (1), is continuously contacted with a dense, non-porous selective membrane (3), such that a permeate (4) is obtained which is enriched in the solute(s) that one aims at recovering, as well as a liquid stream (5) that is depleted by the solute(s) meanwhile removed.

16 – Figure 2 depicts a diagram of a pervaporation unit which is adequate for the recovery of solutes from ionic liquids. Some variations of this type of installation can be considered which will be discussed later in this text. The installation shown in figure 2 consists of a feed reaction vessel (1), which contains the ionic liquid and the solute(s) that one aims at recovering. Using a recirculation pump (2), the content of this feed vessel is fed to the pervaporation module (3) through an appropriate feed tubing (4). The pervaporation module (3) consists of a feed compartment (5), the selected membrane (7) across which the solute(s) desired permeate, and the pervaporate compartment (6). By acting of a vacuum pump (10) the pervaporate is conducted through a vacuum line (8) and captured in appropriate units (11), which can be placed in parallel or in series, before or after the vacuum pump. The pervaporate captured can be removed from these units in a continuous or discontinuous form, by actuating valves or using pumps (12). After contacting the membrane (7), the feed stream is returned to the feed vessel (1) through the recirculation ducts (9).

17 – The feed stream consists of an ionic liquid, or a mixture of ionic liquids, in which are dissolved one or more solutes possessing a measurable vapour pressure and which one aims at recovering selectively. The feed stream may also contain other non-volatile constituents, such as catalysts, bio-catalysts, metals and salts.

18 – As an ionic liquid it is considered any liquid constituted of ions, due to which said liquid lacks a measurable vapour pressure.

19 – The solutes to be recovered consists of any type of solute with a measurable vapour pressure, such as: aromatic compounds, cyclic or aliphatic compounds, esters, alcohols, aldehydes, ketones and acids, and also inorganic compounds such as water, carbon oxides, nitrogen oxides and sulphur oxides.

20 – The feed stream should preferentially be at a temperature lower than 150 °C in the case of using, for example, polymeric membranes that are sensitive to elevated temperatures, but could be processed at higher temperatures when using membranes that are technically stable at these higher temperatures. There are no restrictions with regard to the pressure in the feed vessel and the feed circuit, although the preferential

situation would be to have the feed stream at atmospheric pressure or close to atmospheric pressure.

21 – The membrane used should represent a selective barrier, such that the permeation of ionic liquid, or any other constituent of non-measurable vapour pressure, from the feed-stream is avoided, and should permit the selective permeation of different volatile solutes, present in the ionic liquid, across the very same. The membrane characteristics should permit that the solutes which one aims at recovering possess a high permeation flux and that other volatile solutes which one does not aim at recovering possess a low permeation flux.

22 – The membranes used should be preferentially non-porous in the sense of not possessing pores that are visible with an electron microscope. They can be composed of different materials of polymeric or inorganic nature. They can also be composed of polymeric and inorganic materials. With regard to the structure of the membranes, they can be homogenous or asymmetrical, and they can also be composite membranes in which case they are constituted of different layers of different materials and/or morphologies. Each of these layers may have a thickness different than that of other layers of the composite membrane. In the case of non-porous membranes, at least one of the layers should be of a non-porous structure.

23 – Porous membranes may only be used if their pores were filled with either a liquid phase which may be identical in its compositions to said feed phase or different from said feed phase, or with a gel or a solid phase different from the membrane matrix.

24 – Concerning their chemical nature the membranes may present a hydrophobic character, meaning that they are more permeable to hydrophobic chemical species, i.e., to chemical species that present an infinite activity coefficient higher than unity in aqueous solution. The membranes may also present a hydrophilic character, which means that they are more permeable to water than to organic compounds.

25 – The membranes may be flat sheets or have a tubular geometry, and they may be installed in different types of modules, namely, plate-and-frame modules, spiral-wound

modules, tubular membrane modules, capillary membrane modules or hollow fibre modules.

26 – The feed stream to be processed by pervaporation may be supplied to the pervaporation module in a continuous, semi-continuous or discontinuous mode. The membrane module may be submerged inside the feed vessel, or reaction-vessel, or it can be placed externally as it is shown in Figure 2. The overall system may include one or more modules, arranged in series or in parallel. The membranes from different modules may be identical or different in their nature, and the geometrical configuration of the modules involved may also be identical or different.

27 – The recovery of solutes by pervaporation may be applied to process a feed stream with constant composition, or it may take place to process a feed stream where a chemical, electrochemical or biochemical reaction is occurring, under catalytic or non-catalytic conditions. In the case of catalytic reactions, they may occur in homogeneous or in heterogeneous phase, and the catalysts may be of chemical nature or biocatalysts.

28 – To establish the driving force needed to promote the transport of solute(s) through the membrane, it can be used a gas stream which circulates continuously through the downstream compartment of the membrane module, or it can be established a vacuum inside this compartment by using adequate equipment such as a vacuum pump, as it is illustrated in Figure 2. The value of the absolute pressure in this compartment may be adjusted in order to assure the adequate driving force, needed to obtain the required flux(es) of the solute(s) aimed to be recovered. The value of the absolute pressure in the downstream compartment is, preferentially, between 5 Pa and 20 kPa.

29 – The solute(s) that constitute the permeate stream may be captured and recovered by using appropriate units. These units, which may be 1 or more, may be arranged in series or in parallel and installed before or after the vacuum pump. The capture units may include condensers, if necessary operated at different temperatures, or other systems such as adsorption or absorption units. If necessary, different capture units may be combined.

30 – Aiming to illustrate the present invention, examples on the use of this invention to recover different solutes present in the ionic liquid $[bmin^+][PF_6^-]$, are given. These examples are not restrictive.

31 – Figure 3 shows the evolution of the percentage of recovery (R_i) over time (t) for different solutes: water, chlorobutane, ethyl hexanoate and naphthalene, present in the ionic liquid $[bmin^+][PF_6^-]$. In all cases a non-porous membrane with a total effective area of 0.01 m^2 was used. The feed stream was processed at 50°C and the absolute pressure in the vacuum line was 10 Pa. In all cases the feed solution volume was 110 cm^3 . For the recovery of water from the ionic liquid a composite hydrophilic membrane was used, while for the recovery of chlorobutane and ethyl hexanoate a composite hydrophobic membrane was employed, and for the recovery of naphthalene a homogeneous hydrophobic membrane was utilised. In all examples presented the degree of solute recovery, defined as the mass ratio between the amount of solute recovered in the permeate stream and the initial amount of solute present in the ionic liquid feed stream, was higher than 99.2 %. These examples illustrate the ability to recover solutes quite diverse in their chemical nature, from ionic liquids, by using the process described in this invention employing adequate membranes and selected operating conditions.

32 - Figure 4 represents the evolution of the individual flux (J_i) of each solute mentioned in Figure 3, plotted against their concentration in the ionic liquid (C_{if}). The experimental conditions used during the experiments represented in Figure 4 are the same described previously for Figure 3.

33 - The main advantages of using this invention for the recovery of volatile solutes from ionic liquids are the following: the target solutes may be recovered at moderate temperatures, even if they exhibit a moderate volatility, by using an integrated system design approach considering the following relations: solutes to be recovered / ionic liquid / pervaporation membrane / operating conditions; when operated under moderate temperature this invention allows to recover temperature sensitive solutes and use catalysts and biocatalysts also sensitive to temperature; the process described by this invention has a high energy efficiency, because the energy consumed is expended for transport of the target solutes and their capture; a large variety of different membranes may be employed in this process, allowing for a high degree of versatility and flexibility

and making possible to solve a significant number of different separation problems; this invention may be used for the recovery of solutes during the time-course of chemical, electrochemical or biological reactions taking place in the feed stream, making possible to shift the reaction equilibrium towards the direction of desired reaction products; the present invention does not require the use of additional solvents or external mass agents and, therefore, it does not lead to the formation of subsidiary polluting streams.

CLAIMS

1. A method of recovering at least one volatile solute present in an ionic liquid feedstock, comprising the steps of:

supplying a flow stream of said ionic liquid feedstock containing one or more dissolved solutes and contacting it with one surface of a non-porous membrane, whose permeability to said at least one volatile solute exceeds its permeability to non-volatile compounds, while simultaneously the ionic liquid present in the liquid feedstock does not permeate through the membrane, being totally retained, the permeant solute transported through the said membrane is desorbed from its surface by action of a vacuum established in the downstream side of the membrane or by a stripping gas stream, being the said permeant solute captured and recovered.

2. A method as claimed in claim 1 wherein the feedstock comprises an ionic liquid or a mixture of ionic liquids, which contains at least one volatile solute.
3. A method as claimed in claim 1 to 2 wherein the solutes present in the feedstock may be any kind of solute with a measurable vapour pressure.
4. A method as claimed in claim 3 wherein the volatile solutes present in the feedstock are aromatic compounds, cyclic compounds or aliphatic compounds, esters, alcohols, aldehydes, ketones or acids, or inorganic compounds such as water, carbon oxides, nitrogen oxides, or sulphur oxides.
5. A method as claimed in claim 1 wherein the feedstock contains non-volatile solutes or dispersed compounds.
6. A method as claimed in claim 5 wherein the non-volatile solutes or dispersed compounds present in the feedstock are metals, oligosaccharides, polysaccharides, amino acids, dipeptides, polypeptides, chemical catalysts or biological catalysts.

7. A method as claimed in claim 1 wherein the said membrane is non-porous or, if it presents pores, they are covered by a layer of non-porous material or they are filled with a fluid, or a gel or a solid phase.
8. A method as claimed in claims 1 and 7 wherein the membrane is polymeric or ~~inorganic or comprises both polymeric and inorganic materials.~~
9. A method as claimed in claims 1, 7 and 8 wherein the membrane is homogeneous or asymmetric or composite.
10. A method as claimed in any preceding claim wherein said membrane has a flat geometry or a tubular geometry, being arranged in a plate-and-frame module, in a spiral-wound module, in a hollow fibre module, in a capillary module or in a tubular module.
11. A method as claimed in claim 1 and 10 wherein one or more modules are used, arranged in series or in parallel.
12. A method as claimed in claim 1, 10 and 11 wherein the membrane module(s) is (are) submerged in one or more feedstock vessels or reactors, or it is placed externally to the feedstock vessel(s) or reactor(s).
13. A method as claimed in any preceding claim using one or more feedstock vessels or reactors having independently controllable environments.
14. A method as claimed in claim 1 and 13 wherein the controllable parameters of the feedstock vessel(s) or reactor(s) are the temperature, the pressure, and the kind and concentration of reagents and catalysts.
15. A method as claimed in claim 1 wherein the feedstock stream is fed to the membrane module in a continuous, semi-continuous or batch mode.

16. A method as claimed in claim 1 wherein a chemical, electrochemical or biological reaction takes place in the feed vessel, in a homogeneous or in a heterogeneous phase, under the presence or the absence of chemical or biochemical catalysts.
17. A method as claimed in claim 1 wherein the solute(s) that permeate(s) through the ~~membrane-is(are)-removed-from-the-downstream-surface-of-said-membrane-by~~ applying vacuum in the downstream compartment or by circulating a gas stream in this compartment.
18. A method as claimed in claim 1 and 17 wherein the solutes removed from the downstream surface of the membrane are captured in one or more units, placed in series or in parallel, at any point of the permeate line.
19. A method as claimed in claims 1 and 18 wherein the units used to capture the permeating solutes are of different kind, such as units for condensation, adsorption or absorption.
20. A method as claimed in claims 1, 18 and 19 wherein different combinations of units to capture the permeating solutes are used, and operated under identical or different mode.
21. A method as claimed in claim 1 wherein the solutes recovered by the capturing units are removed in a continuous mode, in a semi-continuous mode or in a batch mode.

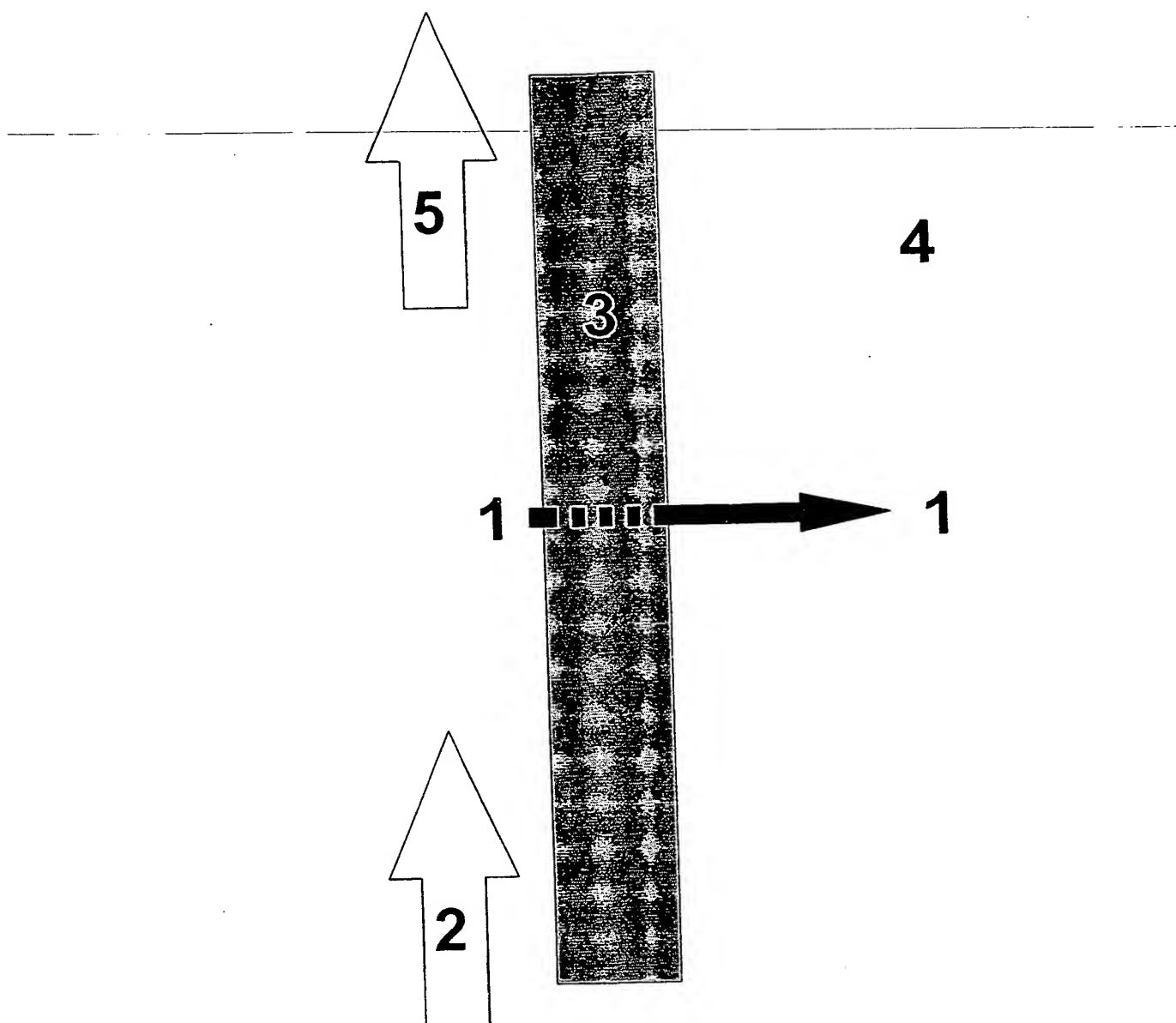


Figure 1

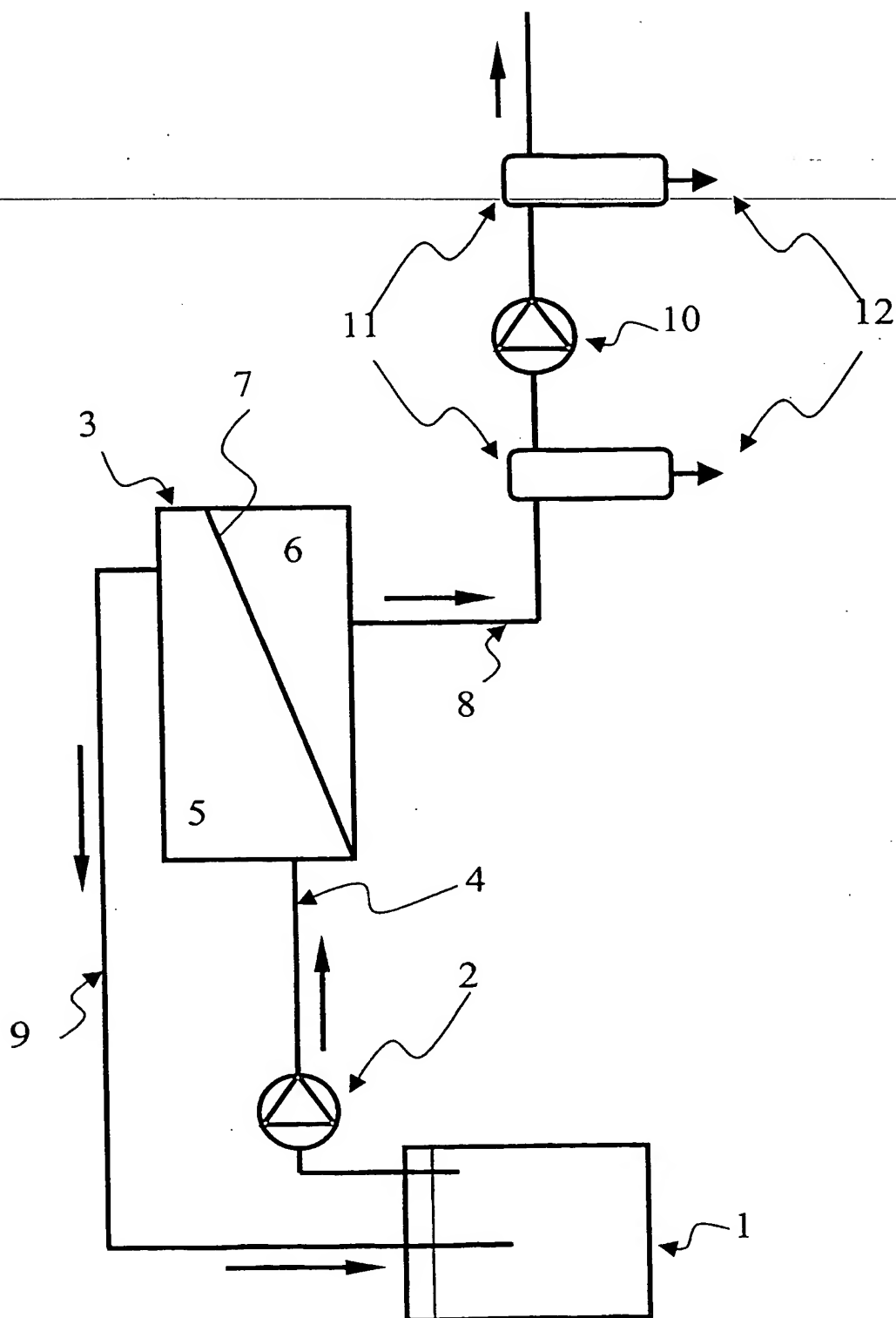


Figure 2

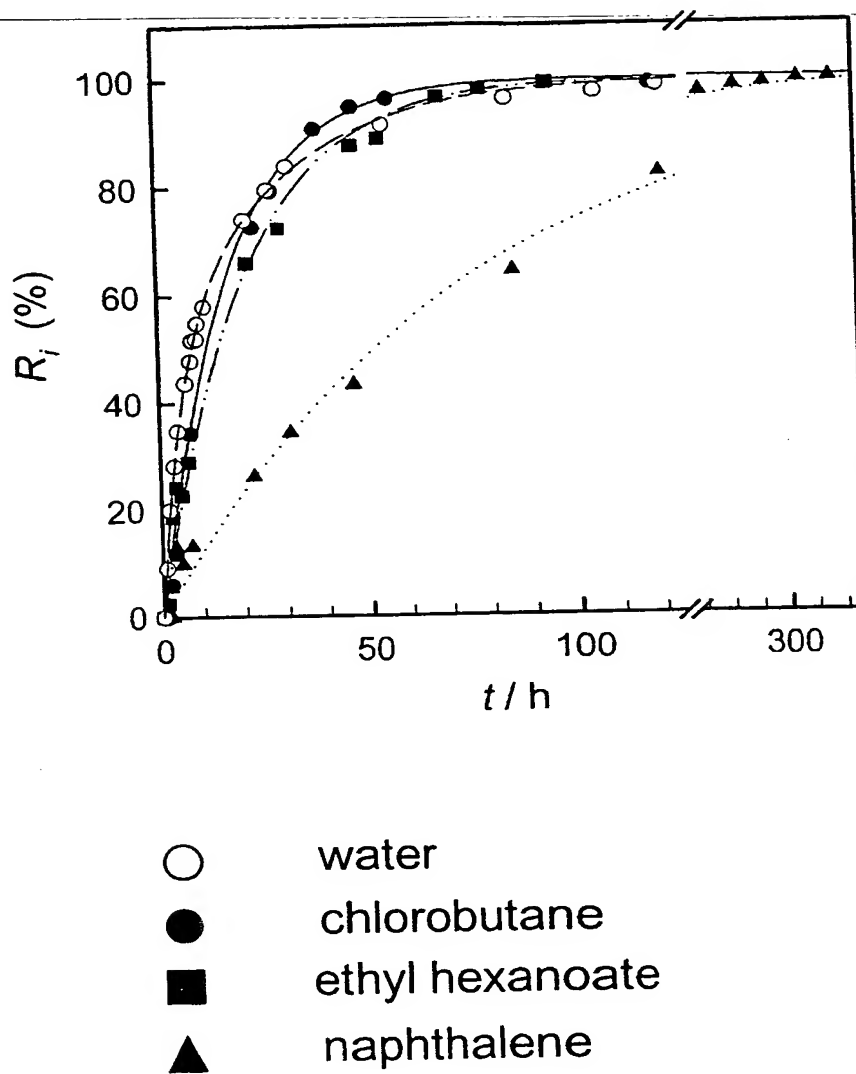
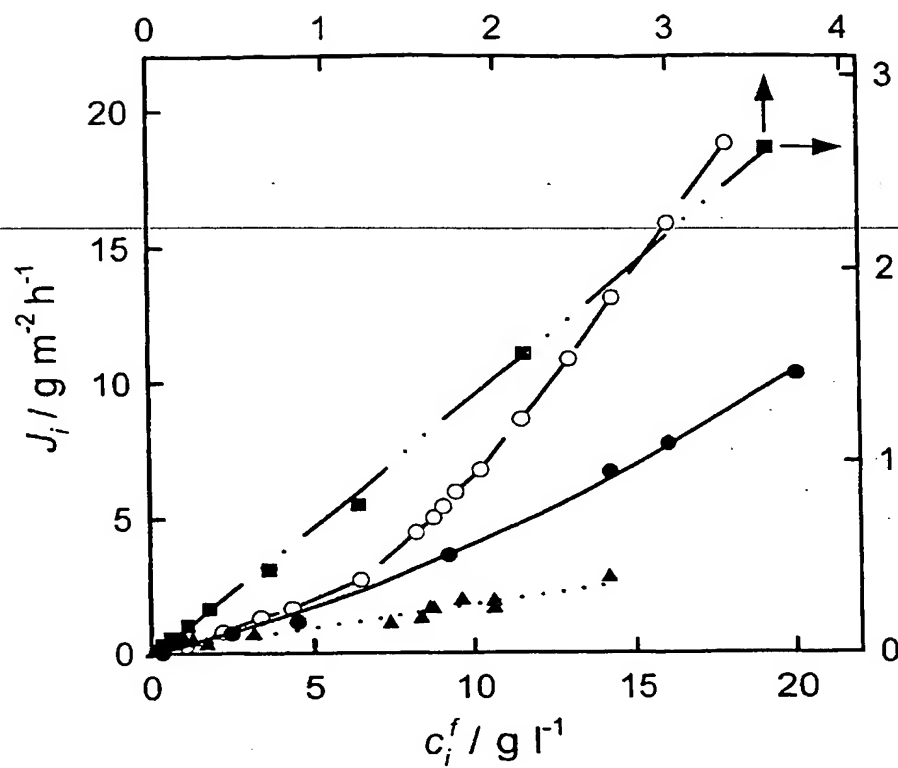


Figure 3



- water
- chlorobutane
- ethyl hexanoate
- ▲ naphthalene

Figure 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/PT 02/00015A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X,P | US 6 273 937 B1 (TRANS IONICS CORP.) 14 August 2001 (2001-08-14) the whole document | 1-21 |
| X | A.G. FADEEV, M.M. MEAGHER: "Opportunities for ionic liquids in recovery of biofuels" CHEM. COMMUN., no. 3, 2001, pages 295-296, XP001120215 cited in the application the whole document | 1-21 |

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